THE ELECTROMOTIVE FORCE OF

CERTAIN ALKALI HALIDE CONCENTRATION CELLS.

by

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THE GRADUATE SCHOOL

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Karr Parker

ENTITLED THE ELECTROMOTIVE FORCE OF CERTAIN ALKALI HALIDE CONCENTRATION CELLS

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF Master of Science

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Recommendation concurred in:

Committee on Final Examination

1. Purpose and Outline of the Investigation.

Although the thermodynamic theory of the electromotive force of concentration cells has been developed for a good many years, comparatively few attempts have been made to investigate salt solutions from this standpoint, and the number of researches the results of which can be used as a basis for the study of the strong binary electrolytes is very small. Among such researches the much discussed work of Jahn* stands foremost. Determinations of the electromotive force of concentration cells of halogen acids have been made by McIntosh* and by Tolman and Ferguson*. Some early measurements were made by Nernst*.

* Z. physik. Chem., 33, 545, (1900)

* J. Phys. Chem., 2, 273 (1898)
*J. Am. Chem. Soc., 34, 232 (1912)

* Z. physik. Chem., 4, 129 (1889)

Two forms of concentration cell have been investigated. The first, of which the following is typical* consists of two

$$Hg \,/\, \underset{\text{solid}}{HgCl},\ HCl\ C_1 \,/\, HCl\ C_2,\ \underset{\text{solid}}{HgCl} \,/\, Hg \qquad A)$$

* In this paper the conventions adopted in the bibliography by Abegg, Auerbach and Luther, "Messungen electromotorischen Kräfte

galvanischen Ketten" will be followed. A vertical line represents a junction; solid-liquid or liquid-liquid. A positive value for the E.M.F. means that current tends to flow from right to left.

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non polarizable electrodes in equilibrium with solutions of different concentrations, which are connected by a liquid junction. These cells, which were employed in Jahn's researches, are usually called "concentration cells with transference".

The second variety, "concentration cells without transference", may be represented by the following example

$$Hg \,/\, HgCl, HCl_{C_1}, H_2 \,/\, Pt - Pt \,/\, H_2, HCl_{C_2}, HgCl \,/\, Hg \qquad (B)$$

These are composed of two independent cells, and involve no liquid junction. This latter type have been the subject of a research by Tolman and Ferguson. McIntosh utilized both kinds in his investigation.

The cells without diffusion are capable of simpler theoretical interpretation, as will be shown in the next section. There is, however, the experimental difficulty of finding a reversible electrode for <u>both</u> the ions of the electrolyte, and for mono-monovalent electrolytes this condition has, so far, been met only in the case of cells involving the halogen acids.

The development of the alkali metal amalgam electrodes by Lewis* and his associates has made it possible to investigate

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* Lewis and Kraus, J. Am. Chem. Soc., 32, 1459 (1900).

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cells of the following form

$$Ag \,/\, AgCl, KCl_{C_1} \,/\, K(Hg)_{x_1}, K(Hg)_{x_2} \,/\, KCl_{C_2}, AgCl \,/\, Ag \qquad (C)$$

a series of which, using various values of the concentrations C_1 and C_2 are dealt with in this paper. Electromotive force measurements on the corresponding cells with transference:-

$$Ag \,/\, AgCl,\ \underset{C_1}{KCl} \,/\, \underset{C_2}{KCl},\ AgCl \,/\, Ag$$

have also been made.

2. Thermodynamics of Concentration Cells.

The thermodynamic differential equations connecting the osmotic work and the electrical energy for the two kinds of concentration cell may be derived most readily by the use of the thermodynamic engine devised by Washburn[1].

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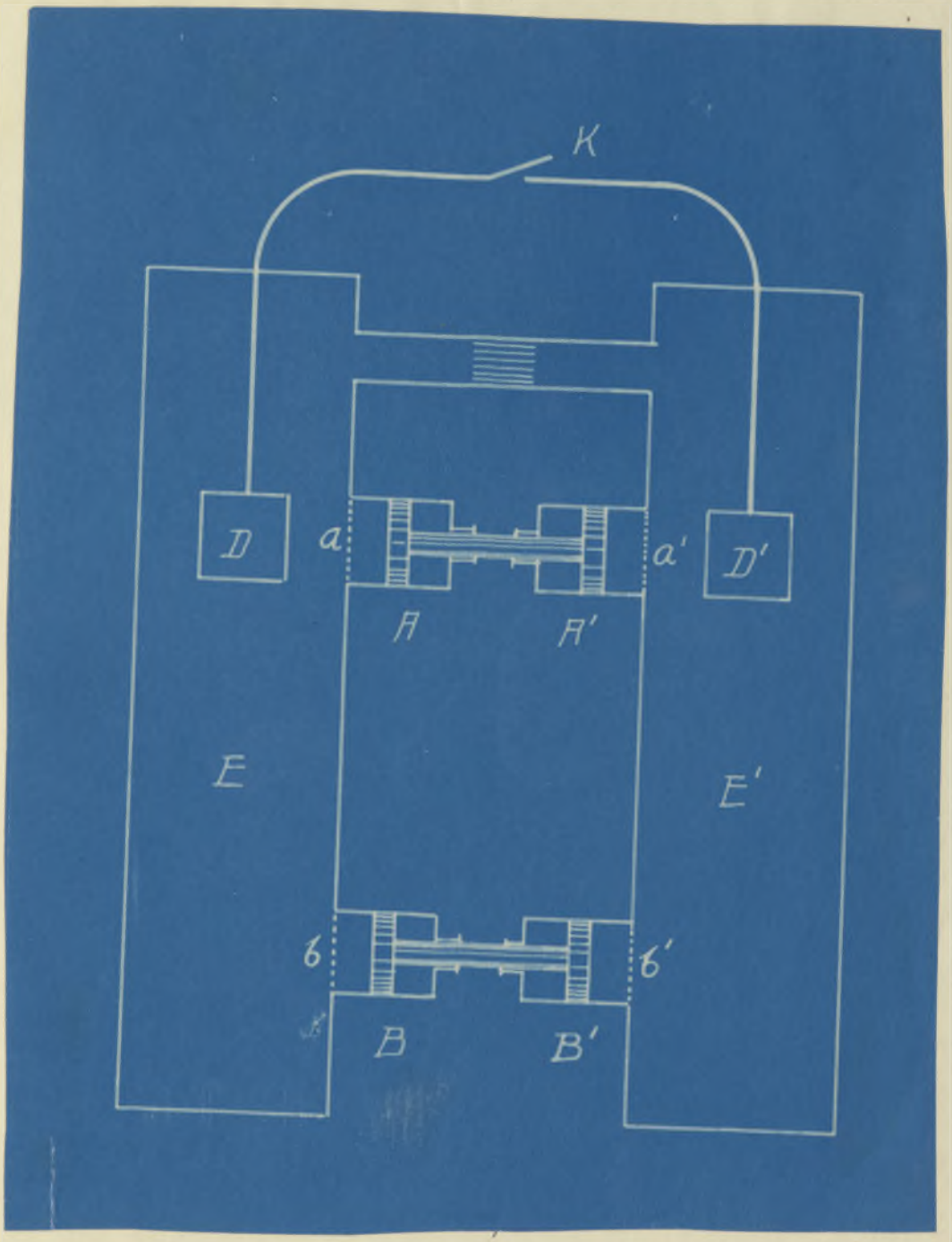
1) J. Am. Chem. Soc., 32, 467 (1910)

Fig. 1 represents the engine used for deriving the equation for the concentration cells with transference. The chamber E contains the salt solution, KCl for instance, at the concentration C. The osmotic pressures of the ions at this concentration may be represented by π_{K^+} and π_{Cl^-}. D represents a reversible electrode, such as silver covered with a layer of silver chloride. The cylinder A is fitted with a membrane a permeable only to the potassium ion at one end. The piston in the cylinder permits the passage of water only. The solution between the piston and the membrane consists, therefore, of a solution of potassium ion in osmotic equilibrium with the solution in chamber E. The membrane ___ is permeable only to chloride ions. The other half of the engine is similar to that just described except that the vessel E' contains the salt at the con-


K
D
a
a'
D'
A
A'
E
E'
b
b'
B
B'

centration C + dC, and the ions have the osmotic pressures π_{K^+} + $d\pi_{K^+}$ and $\pi_{Cl'}$ + $d\pi_{Cl'}$. A movement of the piston A - A' from left to right is, obviously, against the osmotic pressure $d\pi_{K^+}$. An electrolytic connection from the vessels E to E' is afforded by the liquid junction as shown.

If the key K is closed and one equivalent F of electricity is allowed to pass, one equivalent of chloride ion will be formed at the electrode D and a like amount will be removed from the solution be electrolysis at electrode D'. The passage of the electricity across the liquid junction will be accomplished by the movement of N_K equivalents of potassium ion in the direction of the current (from E' to E) and the migration of $(1 - N_K)$ equivalents of chloride ion in the reverse direction, where N_K is the Hittorf transference number of the Kation. Thus the total effect of the operation of the cell will be the transfer of (N_K) equivalents of potassium chloride from the solution of the concentration C + dC to one of the concentration C. To compensate for this change and to maintain a constant difference of concentration the pistons A - A' and B - B' are moved reversibly toward the right, withdrawing N_K mols of each ion from chamber E and forcing them into chamber E'. As the electrical energy must be equal to the osmotic work, the following relation holds:-

$$FdE = N_K (V_{K^+} d\pi_{K^+} + V_{Cl'} d\pi_{Cl'}) \qquad (1)$$

in which E is the electromotive force and V_{K^+} and $V_{Cl'}$ are the volumes of solution containing one gram equivalent of ion.

Fig. 2 is a thermodynamic engine for the cells without transference. It is similar to that shown in Fig. 1 except

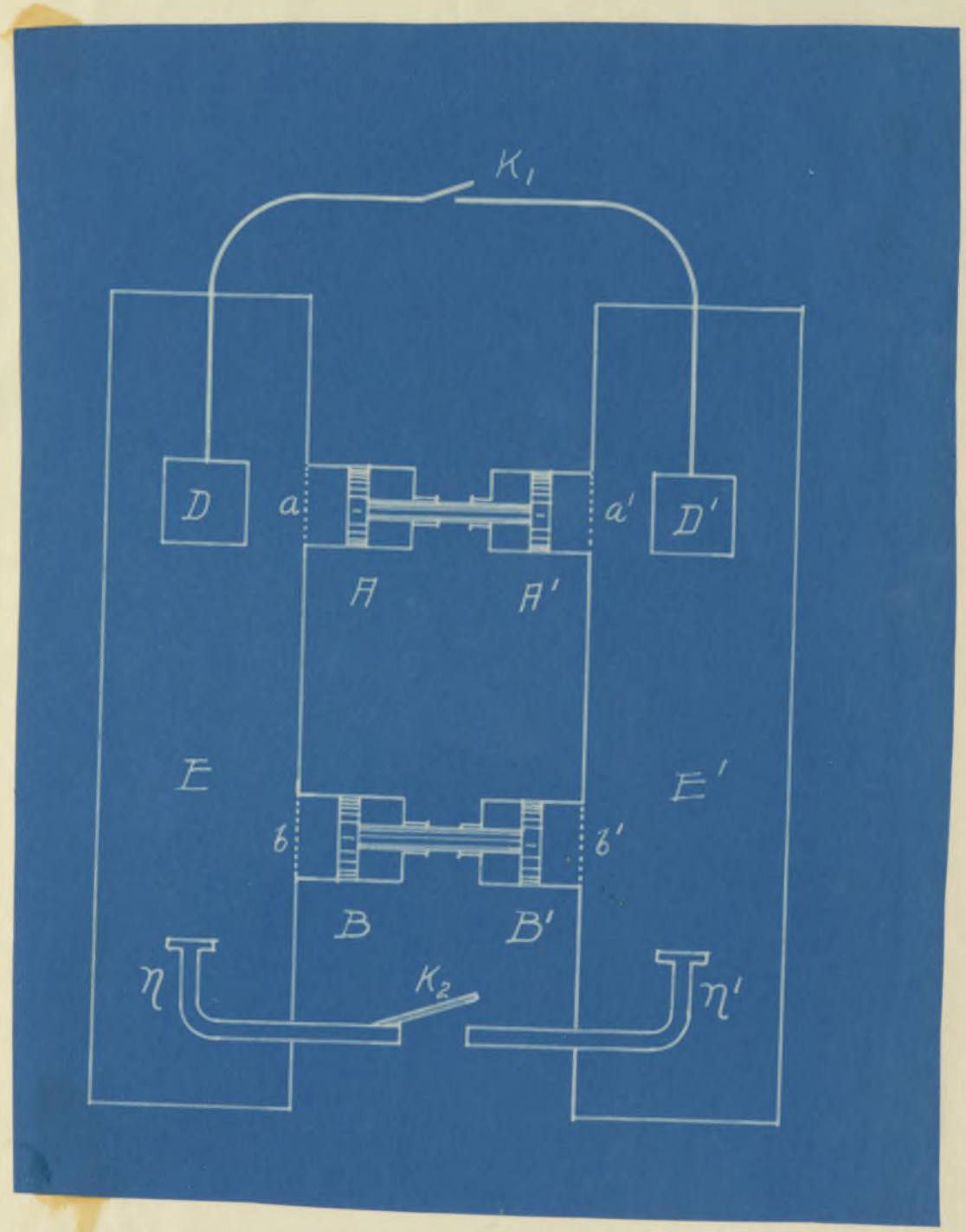


Fig. 2.

that the liquid junction has been replaced by the electrodes N - N', which, in the case under discussion, are potassium amalgam electrodes. The concentrations of the salt are C and C + dC in the chamber E and E' as before. On closing keys K_1 and K_2 and allowing F coulombs to pass one gram equivalent each of potassium ion and of chloride ion will be formed in chamber E and a like amount will be removed by the electrodes from chamber E'. To maintain equilibrium the pistons A - A' and B - B' must be moved reversibly toward the right, each through a volume containing one gram equivalent of ion. Equating the osmotic work and electrical energy we have:-

$$FdE = V_{K^+}\, d\pi_{K^+} + V_{Cl'}\, d\pi_{Cl'} \qquad (2)$$

an expression which differs from (1) only in the fact that it does not contain the transference number N_K. Equations (1) and (2) are as far as we can go using purely thermodynamic reasoning.

If we assume that the ions are normal solutes and the solutions are dilute, i. e. that $\pi = \frac{RT}{V} = CRT$ (C = concentration) hold for each ion, equation (2) becomes $FdE = 2RT\, d\ln C$, which on integration gives:-

$$E = \frac{2RT}{F} \ln \frac{C_i}{C_i'} \qquad (3)$$

for the electromotive force of a concentration cell without transference, in which C_i and C_i' are the concentrations of either ion in the two solutions.

With the further assumption that N_K is independent of the concentration the integration of equation (1) gives the familiar Nernst equation:-

$$E = \frac{2N_K\, RT}{F} \ln \frac{C_i}{C_i'} \qquad (4)$$

Our purpose in making this investigation was to discover how well the theory just outlined applies to concentration cells containing solutions of potassium chloride. The work will be extended to solutions of other alkali halides.

The Concentration Cells Without Transference.

As already mentioned, the concentration cells without transference investigated may be represented by:-

$$Ag \,/\, AgCl,\ \underset{C_1}{KCl} \,/\, K(Hg)_x - K(Hg)_x \,/\, \underset{C_2}{KCl},\ AgCl \,/\, Ag$$

Such cells involve (a) reversible silver-silver chloride electrodes and (b) reversible potassium amalgam electrodes.

(a) Silver halide electrodes have been thoroughly investigated by Jahn[1] and by Halle[2]. In most particulars the dir-

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2,

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ections for their construction given by the latter have been followed. A disadvantage of the forms used by both these investigators was the limited extent of surface exposed to the solution since they were made from a single piece of silver or platinum wire. As the tendency to polarize when small currents are applied, and the electrical resistance of the solid liquid boundary, both decrease with an increase of surface, the electrodes represented by R - E and R' - E' in Figure 1 were used. They consist of a piece of platinum gauze, about two centimeters square, welded to a platinum wire, which made contact with mercury through a seal in a glass tube. The gauze was plated with a thick coating of silver from a $KAg(CN)_2$ solution, using a

current density of about .5 ampere per square decimeter of surface. They were then thoroughly washed and allowed to stand twenty-four hours in pure water. The electrodes were next made anodes in a dilute potassium chloride solution, to which a few drops of hydrochloric acid had been added. After electrolysing five or ten minutes with a current of 5 to 7 milliamperes, the electrodes were covered with a coating of silver chloride, of a reddish brown color, the shade of which was the same whether the electrolysis was carried out in the light or in complete darkness.

Electrodes were made in this manner in sets of eight, forty being used altogether. Electrodes chosen at random from different sets were checked against each other frequently with the result that "normal" electrodes were always found to be within a few tenths of a millivolt of each other. When polarized by the application of one millivolt they returned to their original potential in a few minutes. New electrodes from one set generally showed potential differences of only a few hundredths of a millivolt. There was a slight ageing effect noticed, the older electrodes being electronegative to the newer ones. As this effect was always in the same direction and of the same magnitude within 0.05 m. v. no error arose from this source, since similar electrodes were always opposed to each other.

Whenever electrodes were transferred from a solution of one concentration to that of another care was taken to allow the solution in the pores of the AgCl to reach the same concentration as that of the new solution. The diffusion of the electrolyte out of the AgCl pores is illustrated by the following

test. Electrodes 7 and 8 were removed from a 0.5 N KCl solution and placed in conductivity water with 5 and 6 which had just been taken from a 0.05 N KCl solution. Their potentials rapidly came together as the solution diffused out of the pores of the electrode.

TIME	(5 and 6) positive to (7 and 8) E. M. F. millivolts
1:00 PM	24.5
1:03	16.1
1:06	8.9
1:09	5.2
1:12	3.8
1:15	2.9
1:30	1.2
1:45	1.1
2:50	0.6
3:40	0.5

**Two kinds of abnormal electrodes were encountered (a) those which became abnormal because of the attack of a parasitic mold, and (b) those in which a white allotropic silver chloride appeared to be formed in place of the "normal" plum colored AgCl.

(a) Some of the electrodes were attacked by an organism after some weeks altho the solutions in which they were placed were made up from sterile conductivity water and pure KCl. The electrodes so attacked invariably became electrically different from the "normal" elements, developing in some cases a potential difference as high as 10 mv. This potential difference was always in the same direction, negative to the "normal" electrode. This mold was investigated by Dr. F. L. Stevens of the Botanical Dep't. University of Illinois and, altho conditions were very unfavorable for its development and culture, was identified as a parasitic mold (Aspergilna). The explanation of this phenomenon would be very interesting.

(b) The second class of "abnormal" electrodes appeared to have an allotropic form of AgCl on their surface. This form of AgCl, white in color and unaffected by light even after weeks of exposure, sometimes appeared in spots on a "normal" electrode and sometimes covered the entire surface. These electrodes were always electronegative to the "normal" electrodes by varying amounts. The elements were all prepared under like conditions and the reason for the development of this modification of AgCl on some electrodes and on certain spots on a "normal" electrode is unknown.

(b) The alkali metal amalgam electrode which is represented by X in Fig. 1 used in this investigation differs from that used by Lewis and his associates only in having two capillary outlets

J and J' for the amalgam, in order that it could be used in the two half cells at one time. To fill the electrode cell with the amalgam the amalgam reservoir shown in Fig. 2 was inverted and connected by a T tube to O in Fig. 2. The other branch of the T tube was then connected to the Gaede pump. After exhausting, and thoroughly drying the amalgam was run from the reservoir, after which carefully dried, pure nitrogen was introduced through the tube marked N_2. The surface of the amalgam either remained bright after the introduction of the N_2 or else an exceedingly thin film slowly formed.

The potassium amalgam was prepared by a method which is a simplification of that used by Lewis and Kraus[1]. A diagram

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1. J. Am. Chem. Soc., 32, 1459 (1910)

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of the apparatus is shown in Fig. 3. It consisted of a distilling flask onto the neck of which a tube with the stopcock was sealed. A capillary tube, P, of about .4 mm. bore, was sealed at one end to the delivery tube of the flask and at the other end to a tube (M) with an internal diameter of 6 mm. Pure mercury was first poured into the carefully dried apparatus. Pellets of potassium were then placed in the tube M which was then fused together at upper end. It was found that these pellets can be most conveniently made by forcing a cork borer into a piece of the metal and then pushing the resulting small cylinder directly into the tube M by means of a closely fitting glass tube. The surface of the metal obtained by this means was covered with a very thin film of oxide. The whole apparatus was next evacuated

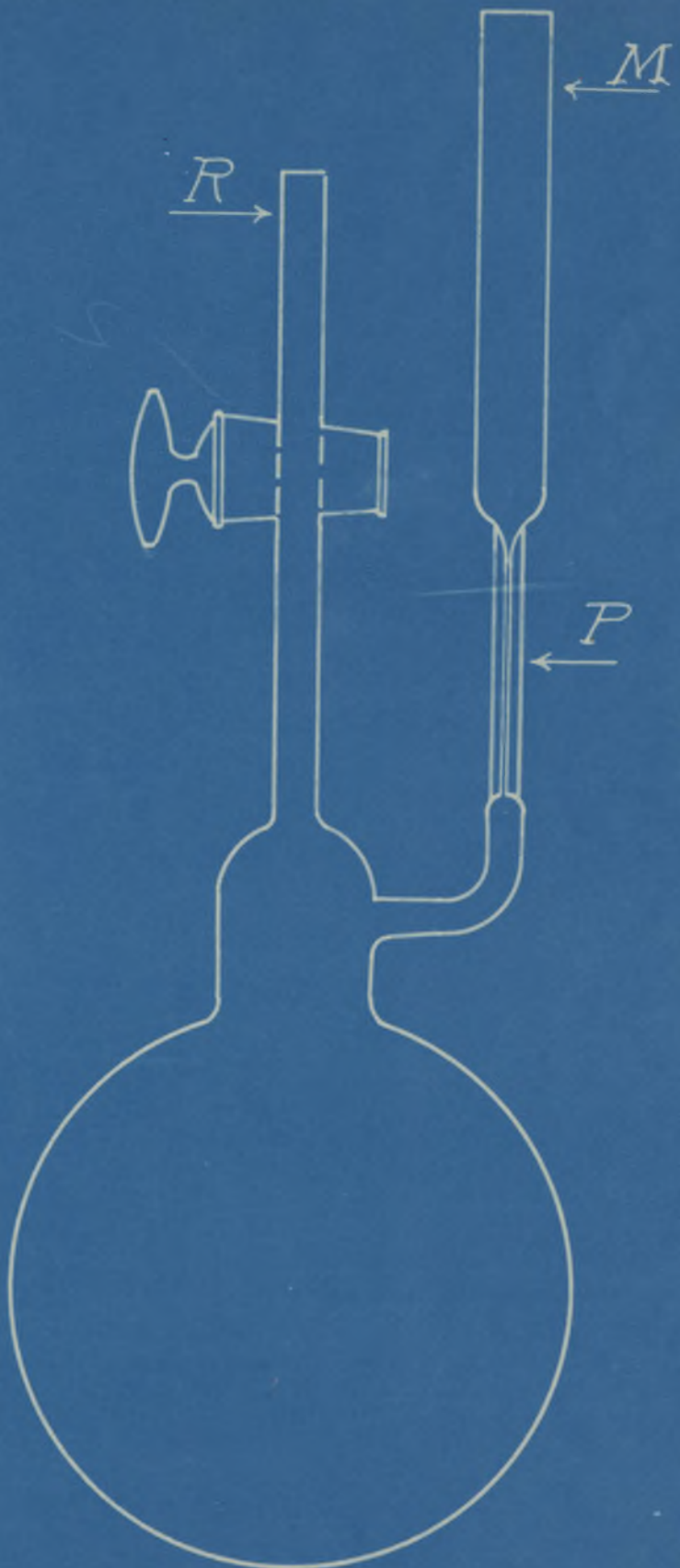

Fig. 3.

through the tube R by means of a Gaede pump. The pumping was continued for half an hour or more, during which time the apparatus was warmed with a flame to remove the last traces of air and moisture from the mercury, after which the side tube from M to D was slowly and uniformly heated with a small free flame, and the potassium soon melted and passed through the capillary, collecting as a brilliant spot of metal in the bend of the tube at C. The capillary was then sealed off at P and the whole apparatus inverted, thus bringing the potassium and mercury into contact. The amalgamation took place quietly, little heat being evolved. When solution was completed, the apparatus was shaken for some time to be sure that the resulting amalgam was uniform. In appearance the surface of the amalgam was as bright as the mercury from which it was prepared. Amalgams of various concentrations were prepared from the stock amalgam by diluting, in vacuo, with pure mercury.

Design and Operation of the Cell.

The apparatus for the concentration cell without transference is shown in Fig. 4. The design finally adopted is the result of considerable preliminary experimenting, since it was found that there were a number of obstacles in the way of realization of complete reversibility at the amalgam electrode. One of the greatest difficulties was the side reaction:-

$$2K + 2H_2O = 2KOH + H_2$$

If this takes place a rapid drop of the potential between the electrode and solution must follow, since the concentration of the amalgam thereby is lowered and the ion concentration in the

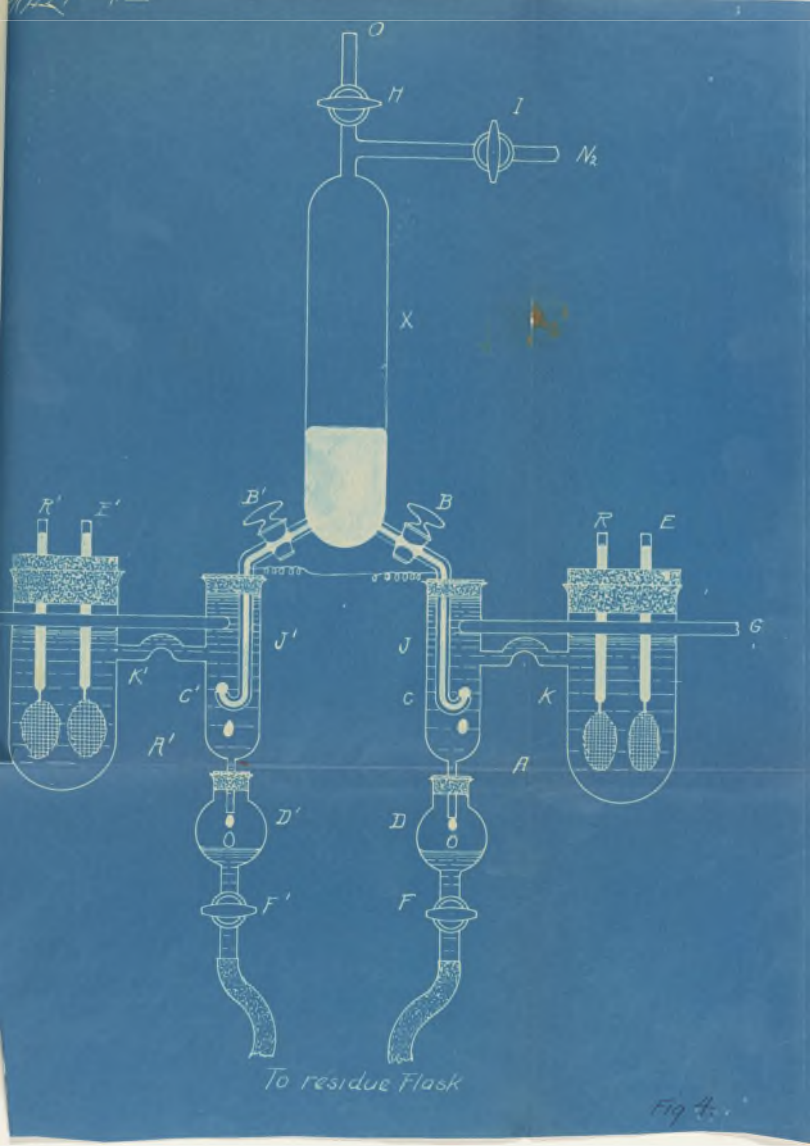

Fig 4.

immediate vicinity is increased. This difficulty was, it is believed, entirely overcome by having a constantly moving amalgam. The arrangement of the cell also permits the immediate removal of the drops of amalgam as they get detached since they fall directly into bulb D and thence into the residue flask. Streams of fresh solution, run in through the tubes G and G' were made to pass by the amalgam electrodes. This made sure that no measurements were carried out with solutions uncontaminated by the passage of the amalgam. The air spaces in the bulbs D and D' permitted the worker to observe the rapidity of the flow of the solution and prevented short circuiting through the rejected material or through the thermostat water. It was found that readings of the voltage of this cell became constant within about .05 millivolt when the flow of amalgam was about thirty drops per minute. After this ~~number~~ an increase in the rate of flow had no influence on the results. The speed of flow of the solution was also found to have no influence, above a certain minimum. These facts tend to show that the side reaction given above was eliminated by this device and also that the amalgam had time to come to electrical equilibrium in the short time that it was in contact with the solution. The formation of hydrogen was never observed in the cell, even when very few drops of amalgam per minute were passing.

Another side reaction, which was more difficult to deal with, will be discussed below.

The arrangement of each half cell in two portions C,K and C',K' made it possible to leave the Ag, AgCl electrodes in contact with solution with which they were in equilibrium and

which was not disturbed by the flow in the adjoining portion. The tube connecting the two portions was bent as shown to prevent mixing.

Early in this investigation it was recognized that oxygen dissolved in the solutions can influence the results on account of the side reaction:-

$$K_2 + O + H_2O = 2KOH$$

and for this reason the solutions were prepared so that they came in contact with the air for a very short time. The effect of this side reaction is the same as the previous one, i.e. to lower the electromotive force, since the addition of potassium ions to both solutions will lower the ratio of the concentrations.

The solutions were made at first by collecting the water very hot in "resistanz glas" bottles from the still used for preparing conductivity water, pumping out the air remaining above the water and replacing it by pure nitrogen. The correct amount of salt necessary to make a solution of the required strength (in mols per liter) with all weights calculated to vacuum standard, was then added in a small glass capsule and allowed to dissolve. A small amount of air was carried into the solution in this last operation. Table I gives measurements of the E. M. F. of the cell:-

$$Ag \,/\, AgCl, \underset{.05\ N}{KCl} \,/\, KHg_x - KHg_x \,/\, \underset{.005\ N}{KCl}, AgCl \,/\, Ag$$

the solutions in which were made as has just been described:-

TABLE I

	Conc. of Amalgam	E.M.F. volts
1)	.02 o/o Approx.	+ .10603 ± .00001
2)	.002 o/o "	+ .10600 ± .00001
3)	.0002 o/o "	.1060 ± .0005

The figures indicate that the electromotive force is independent of the concentration of the amalgam within wide limits. The amalgam in determination number 3 was too dilute to allow accurate measurements to be made. These readings are, however, about four millivolts too low as further measurements have shown. Apparently the small amount of dissolved oxygen reacted instantaneously with the amalgam, lowering the potential at both amalgam solution boundaries, as can be seen, the effect is surprisingly constant. The final measurements were made using solutions from which every trace of oxygen was excluded. The apparatus used for preparing such solutions is shown in Fig. 5. The stopper of the "resistanz glas" bottle A carries two tubes. Tube B which reaches to the bottom of the flask is used for the delivery of the solution to tube G of Fig. 1. Tube C - C' is in two parts, which may be shut off from each other by a rubber tube, and a pinch cock, represented by F. Both parts are fitted with stopcocks, as shown. In making the solution the water is collected by placing the outlet from the still well within the mouth of the bottle and regulating the flow through the condenser so that the water is collected as hot as possible and a large volume of steam is evolved. When the bottle is nearly full, the stopper is inserted, the tube B filled with water, and the water boiled for fifteen or twenty minutes by evacuating through the outlet from tube C. After this pure nitrogen was run in through this tube and the water allowed to cool with a pressure of this gas upon it. The required amount of salt was then weighed out into the capsule E and placed above the pinch cock in the tube C', which is then

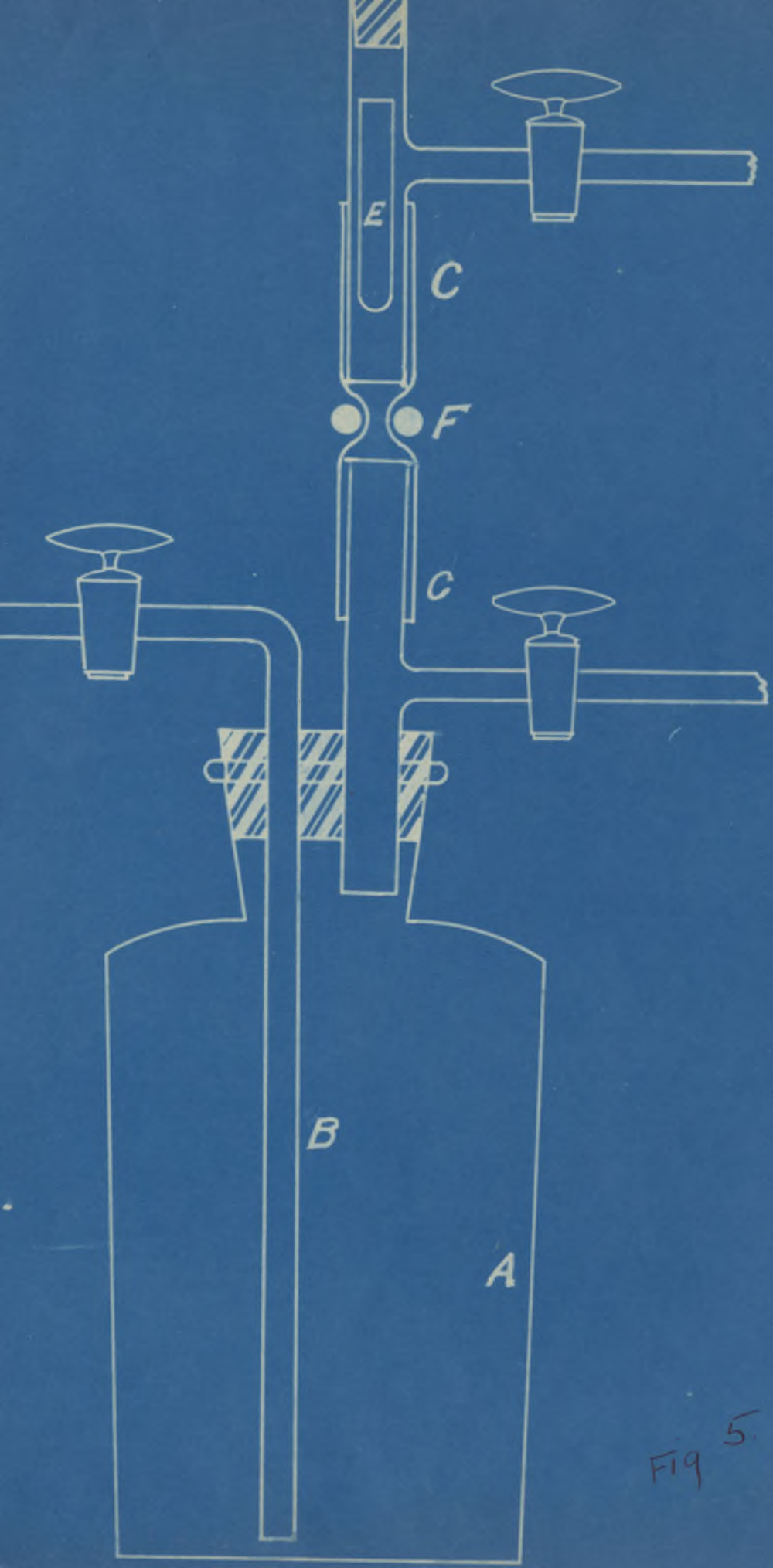

Fig 5.

closed at its upper end. The air was removed from this space be evacuating and replacing with nitrogen several times and the capsule was made to drop into the water by opening the pinch cock F.

Table II give a summary of the results obtained from cells in which solutions used were prepared in the manner just described.

TABLE 2.

Electromotive Force of Potssium Chloride Concentration Cells without Transference at 25°.

Ag /	AgCl, solid	KCl /	K_xHg - K_xHg	/	KCl,	AgCl	/	Ag
		0.5 N	.02 o/o		0.05 N	"		- .10735
	"	0.5 "	.002 o/o		.05 N	"		" - .10745
	"	.1 "	.004 o/o		.01 N	"		" - .10885
	"	.1 "	.002 o/o		.01 N	"		" - .10900
	"	.05"	.004 o/o		.005 N	"		" - .11085
	"	.05	.002 o/o		.005N	"		" - .11085

The Amalgam Concentrations are approximate.

The Concentration Cells with Transference.

Cumming and Gilchrist[1] have described the best conditions for the formation of liquid junctions giving reproducible results. These are (a) the use of wide tubes in making the connections, (b) the formation of a new boundary shortly before the measurements are tkaen, (c) the mechanical mixing of the solutions at the boundary. The cell used for this purpose in this investigation is shown in Fig. 6. The vessles M and M' contain the identical silver, silver chloride electrodes used with solutions of the corresponding concentrations in the cells without transference. The tubes L and L' of about 5 mm.

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1. Trans. Farad. Soc., 9, 174 (1913)

internal diameter are brought together in the small vessel K which contains a solution formed by mixing together equal parts of the solutions contained in M and M'. The tubes can be readily filled by pressing the rubber stoppers deeper into the vessles M and M' or by placing a slight air pressure on the surface of the solutions by means of tubes (not shown) through the stoppers. The "time change" which apparently always present where a liquid junction is involved, was only one millivolt per hours, and as new boundaries which gave the original reacing could readily be obtained, it is believed that maximum values of the electromotive force were measured in each case.

The results of these measurements are given under Table 3.

TABLE 3.

Electromotive Force of Potassium Chloride Concentration Cells with Transference at 25°.

Ag	/	AgCl,	KCl	/	KCl	/	AgCl	/	Ag	
"		solid	0.5 N		.005 N		solid		"	- .05357
"		"	0.5 "		.005 "		"		"	- .05357
"		"	0.1 "		.01 "		"		"	- .05400
"		"	0.05"		0.005 "		"		"	- .0547
"		"	.05"		.005 "		"		"	- .05475
			.01		.001					

Purification of Materials. Mercury. The Mercury used in this investigation was purified by passing it in a thin stream through a tube, a meter long, filled with dilute nitric acid and then distilling with diminished pressure in a current of air.

Potassium chloride. Kahlbaum's best grade of potassium chloride was recrystallized one or more times from conductivity water, and the mother liquor drained off with the help of a centrifuge. It was always fused immediately before using.

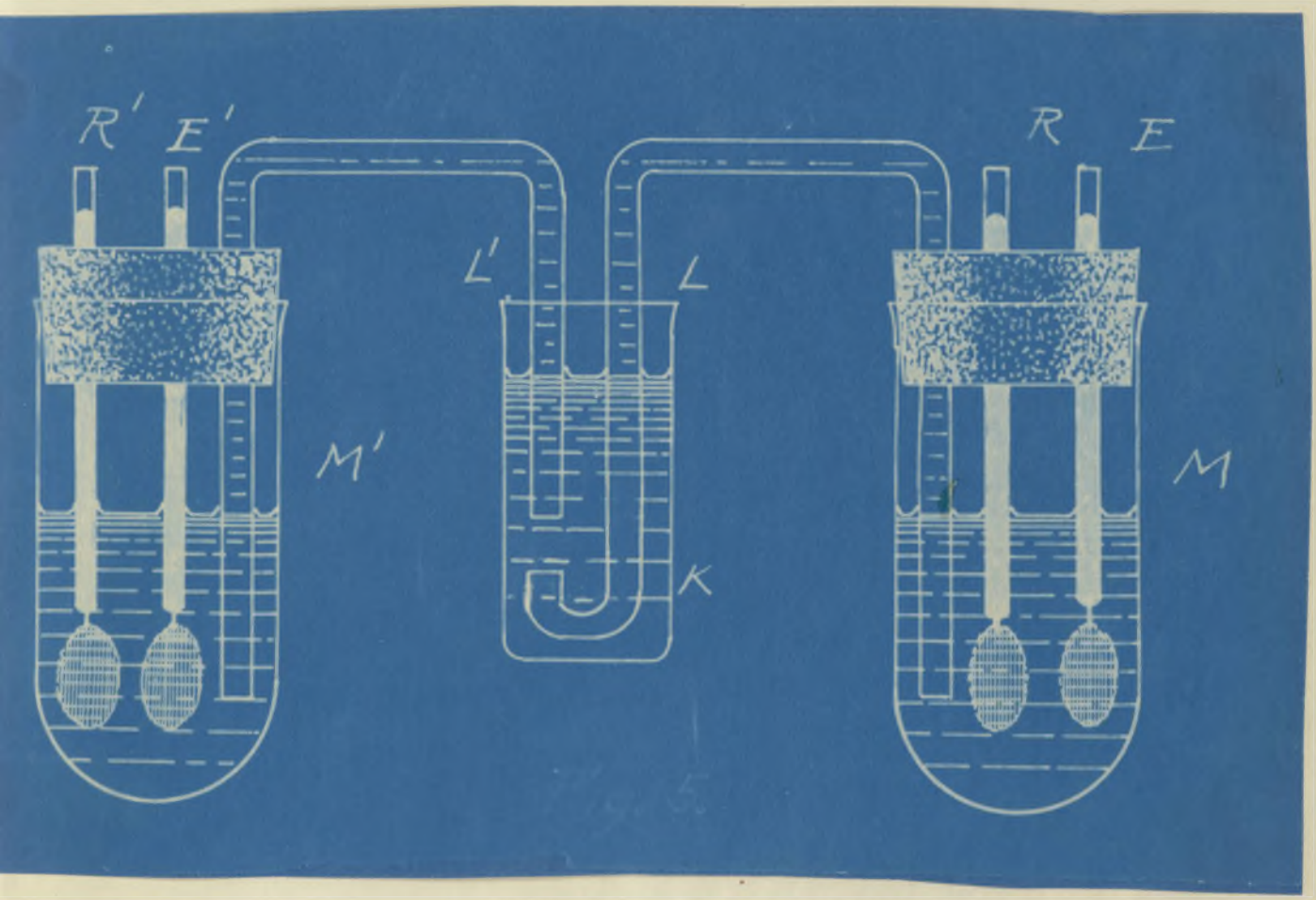

Fig. 6

Nitrogen. Since all of the operations carried out in this work were found to be disturbed by the presence of oxygen, in even very small amounts, a rather large volume of an inactive gas were found to be a necessity. Nitrogen was found to fill all the requirements. It was prepared from sodium nitrite and ammonium chloride as described by Tucker and Lampen and kept over water in a gasometer. To remove the small amount of oxygen remaining, as well as the moisture present, it was passed through a train consisting of sulphuric acid, soda lime, copper heated to redness, and finally, in certain cases through U tubes filled with P_2O_5. The copper which had been reduced by hydrogen from copper oxide was contained in a quartz tube. This was a convenience as it could be heated and cooled rapidly without danger of breaking.

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*Orig. Comm., 8th Int. Cong. App. Chem. 21, 121 (1912)

Discussion of Results.

On page 5 we obtained the differential equation $FdE = n(\pi_1 d_{v_1} + V_2 d\ \pi)$ connecting the osmotic pressure and the electromotive force of a concentration cell with transference, and the expression $FdE = V_1 d\ \pi + V_2 d\ \pi$ for a concentration cell without transference. From this it is apparent that, whatever the relation between π and V may be, the ratio:-

$$\frac{\text{E. M. F. of cell with transference}}{\text{E. M. F. of cell without transference}}$$

should be equal to the transference number of the kation. This, of course, involves the assumption, that thermodynamics can be used in deriving relations for cells in which the unstable liquid junction is used. Table 4 gives values of this ratio and also the usually accepted values of the transference number.

TABLE 4

Concentrations	E. M. F. ratio	Transference Numbers from E.M.F. meas.	Direct determination
.5 - .05	$\frac{53.57}{107.4}$	.498	.496*
.1 - .01	$\frac{54.00}{108.9}$	.496	.496
.05-..005	$\frac{54.7}{110.85}$	.494	.495'

* .2 N
' Value at infinite dilution, also "true" transference

From these results it can be seen that, for this salt at least, the thermodynamic theory as outlined is valid within the experimental error. This method of determining the transference number was suggested by Helmholtz, and has been tried experimentally

but without success, for the transference number of the hydrogen ion in hydrochloric acid by McIntosh*.

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* l. c.

On applying the integrated equations (3) and (4) to the data we do not find the same agreement of the theory with the results of experiment. In column 2 of Table 5 may be found values of the ratio of the ion concentrations in the two solutions C_i/C_i^1 calculated from the conductance data of Melcher*.

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* J. Am. Chem. Soc., 33, 1668 (1911).

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and in column 3 may be found values of the same ratio calculated from the equation for the electromotive force of the cells without transference:-

$$E = \frac{2RT}{F} l u \frac{C_i}{C_i'}, \qquad (3)$$

TABLE 5

Concentrations	C_i/C_i' from conductance measurements	C_i/C_i' from E.M.F. measurements
.5 - .05	8.85	6.61
.1 - .01	9.15	7.10
.05- .005	9.30	7.60

Assuming that equation 3 can be used to determine ratios of ion concentrations, it is apparent that the conductance method yields too high degrees of dissociation in the more concentrated solutions. Jahn, reasoning from sililar data to this came to the conclusion that the ions move more rapidly as the salt con-

centration increases. A more probable explanation is that the osmotic pressure of the ions is not directly proportional to the ion concentration as is assumed to be the case in the integration of equation (3), but is a more complicated function of the number of ions present in solution. This subject will be much more fully discussed in later papers on this subject.